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REPORT NO. MR 59-2
DATED: 29 Aug. 1962

MANUFACTURING RESEARCH - BONDING -
CERAMIC-TO-METAL

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Contract No. AF33(657)-7248

GENERAL DYNAMICS | FORT WORTH

A DIVISION OF GENERAL DYNAMICS CORPORATION
(FORT WORTH)

Department 6
FWP 1971-9-54



TEST: F-8380

MODEL All

REPORT MR 59-2

DATE 23 December 1959

TITLE

MANUFACTURING RESEARCH -BONDING - CERAMIC-TO-METAL

SUBMITTED UNDER

Manufacturing Research Project MR59-2

The tests described in this report were conducted between 1 February 1959 and 10 December 1959.

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NO. OF PAGES 36

NO. OF DIAGRAMS 12

REVISIONS

[illegible]

CONVAIR

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(FORT WORTH)

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MODEL A11
DATE 23 December 1959

A C K N O W L E D G M E N T S

Acknowledgement is given to the following persons
whose knowledge, advice, and help have contributed
to this project:

J. M. Warren

F. E. Hancock

L. G. Incapreria

C. J. Kastrop

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MANUFACTURING RESEARCH - BONDING - CERAMIC-TO-METALSUMMARY OF RESEARCH INFORMATION

This report covers the work conducted during the first year of a three year program outlined in FMRP-020 to investigate ceramic-to-metal bonding and ceramic adhesives for metals. Since the project was stopped after one year of work, this also constitutes the final report. The goals outlined for the first year of work were achieved. Successful ceramic-to-metal attachments were made by use of brazing alloys and by mechanical means. The attachment of metal-to-metal with ceramic adhesives was also attained.

The major portion of the effort in this project was direct experimentation conducted in the Engineering Chemistry Laboratory. Small specimens of ceramics and metals were bonded and brazed together and tested in an effort to find a satisfactory ceramic-to-metal bonding or brazing technique. The strength of these bonds was tested at room temperature, 1200° and 1500°F. Some of the brazed specimens exhibited a room temperature tensile strength of 11,000 psi and 5,000 psi when tested at a temperature of 1500°F. The majority of fractures at all temperatures on the brazed ceramic-to-metal test specimens occurred at the ceramic-metallized interface or within the ceramic itself.

Several ceramic adhesives were employed in efforts to bond various combinations of small specimens of alumina, pyroceram, Rene'41, Kovar "A" metal, RS-140 titanium, and 17-7 PH stainless steel. These specimens were tested at room temperature, 600, 800, and 1000°F. 17-7 PH stainless steel bonded with UI-1067-1A ceramic adhesive resulted in a shear strength of 1900 psi when tested at either room temperature or 1000°F.

The actual laboratory work was preceded by a literature survey and systematic study aimed at selecting the most likely materials and bonding or brazing techniques. The very latest ceramic adhesives developed under recent Air Force contracts were used in this project and many of the successful ceramic-to-metal brazing techniques currently employed in the electronic industries were adapted to this project.

A 0.50" x 8.0" x 12.0" pyroceram 9606 plate was mechanically attached and sealed to a chamber made from 17-7 PH stainless steel so that the ceramic became one side of the chamber. The chamber was pressurized with air and subjected to temperatures up to 1500°F. The ceramic successfully withstood the maximum temperature and no failure was observed after being subjected to 3.5 psi at 1500°F. This larger size test specimen and test jig was designed for the purpose of investigating the problems of attachment of larger size ceramic specimens.

A limited study was conducted in the laboratory on the metallizing of alumina by various methods. Several of the processes (especially the active hydride and the electroless nickel plating processes) looked promising. A number of small specimens prepared by these methods were experimentally investigated in the laboratory.

The results of this research program show that ceramics can be successfully brazed to metals, and that the assemblies are capable of withstanding 1500°F with fair to good strength. It is recommended that further research be continued at Convair to determine or develop the following: (1) the size-strength relationship of ceramic-to-metal attachments by fabrication of larger test specimens, (2) the merits of the active metal and hydride processes and the electroless nickel process for metallizing various ceramics for subsequent brazing to other metals and ceramics, and (3) brazes capable of exhibiting good strength at temperatures up to 2000°F.

MANUFACTURING RESEARCH - BONDING - CERAMIC-TO-METAL

INTRODUCTION AND THEORY 1 Through 16

One of the more difficult problems which must be overcome if ceramics are to be used as structural or insulating materials on aircraft is the problem of attachment. This research program included a brief literature survey of the problem, followed by an investigation of ceramic-to-metal attachments by use of (1) ceramic adhesives, (2) brazing alloys, and (3) mechanical means.

Some of the first ceramic-to-metal bonding investigations were made during the development of the electric light. Tungsten, molybdenum, and platinum were used as the filament or lead-in materials. At that time there were many glasses whose thermal expansions closely matched these metals. The metals usually oxidized slightly when touched by the molten glass. The oxides adhered to the metals and were wetted by the glass, making a satisfactory seal.

Weyl¹ states that four types of materials will adhere to glass: (1) a compatible ionic or a compatible randomly arranged material which adheres because the same forces exist in both media, e.g. fluoride coated glasses, (2) a material which is incompatible with glass but which can react chemically with glass e.g. organosilicon chlorides, (3) materials which allow the formation of an intermediate layer, e.g. the metallic oxide film responsible for the adherence of iron-nickel-chromium alloys, and (4) materials which are not included above but adhere because of dispersion of van der Waals forces, e.g. safety glass interlayer material. The third class of materials were used in this investigation.

Glass to metal seals consist essentially of three components: the glass, the metal, and a thin layer of oxide on the metal surface at the glass-metal boundary. Perhaps the most important factor in the selection of the metal is its thermal expansion. If the thermal expansion of the ceramic and metal are not closely matched, thermal stresses develop on solidification and subsequent cooling of the bonding material. When the mis-match of expansions is great, the stresses exceed the strength of the bond, and the joint will fail. The oxide layer is also a critical part of the bonding and care must be exercised in preventing the layer from becoming too thick when making the seals. The oxide layer is influenced not only by the metal and its treatment, but also by the glass composition. In keeping the film thin (but not too thin so as to introduce small gas bubbles at the glass-metal interface) the strength of the seal may be made stronger. The weakest link in seals of this type is the adhesion of the metal to its oxide. It is believed by some investigators that the first few atomic layers of the oxide have the same lattice dimensions as the base metal, so that there is no discontinuity.

Glass to metal seals can be broken down into two general types, i.e. matched and mis-matched seals. As the name implies the mis-matched seal occurs when the glass and metal have different values of thermal expansion. The seal is designed so that the glass will be in slight compression when cooling. An important factor in this type of seal is that the metal must (1) be very thin compared to the glass and (2) exhibit a very low yield strength. Housekeeper² is responsible for the technique which employs the use of a metal section (brought down to a feathered edge of only a few mils thickness) at the seal. The strength of this thin section is so low that it will compensate for the differential expansion between the metal and glass through its plastic flow without overstressing the glass. The metal, which is usually copper, can be sealed to both low- and high- expansion glasses. Obviously this type of seal can only be used in applications where high strength is not essential.

In making a matched seal, an attempt is made to select the glass and metal combination so that, upon cooling, there is no stress (or only slight compression stresses) set up in the glass. Figure 1 shows the relative expansion values for several ceramics and metals at various temperatures. The metal in a matched seal should have a higher overall expansion than the glass. This is because the expansion of the metal is generally straight whereas that of the glass is not. Glasses generally undergo an increase in expansion at temperatures above their lower annealing temperature. As the seal cools the glass becomes increasingly viscous until it is no longer able to flow enough to overcome differences in expansion which may occur during the cooling. This "stiffening" of the glass occurs within the annealing range. Therefore, it is important that the expansion selection be made within the temperature limits bounded by room temperature and the annealing temperature, not necessarily the overall range reported in most of the literature. Kovar (42% nickel, 5.5% chromium, 52.5% iron alloy) metal, however, has a thermal expansion change much like glass (see Figure 1) and is widely used in matched seals because of this property.

In all ceramic-to-metal bonds there must be a transition area of some type. There are three general methods used to bond ceramics to metals. These are (1) use of glass adhesives, (2) use of cements, and (3) use of brazing alloys. Glass adhesives and cements are limited because of the brittle nature of the bonds produced and the necessity of very closely matched thermal expansions. The mechanism of the glass bonded seal is that the glass adheres and takes into solution a small amount of the ceramic and the oxide film on the metal, thus creating a bond. In the cemented bond, almost all the strength is attributed to mechanical gripping of the surfaces only.

The brazing (or soldering) method gives a bond of greater mechanical strength and ductility. As a rule the ceramic must be metallized before it can be brazed or soldered. There are several methods by which the metallizing may be accomplished. These include (1)

firing a metal oxide on the surface of the ceramic, then reducing the outer layer of the oxide, (2) mixing, forming, and firing ceramic and metal powders together to form a metal phase, (3) metallizing by active metal or active metal hydride process, (4) glazing the ceramic with a metal containing glaze, then firing in a reducing atmosphere (or at times an oxidizing atmosphere), (5) metallizing with refractory metal powders, (6) metallizing directly to ceramic with no transition layer, (7) vapor depositing metal coating, (8) flame spraying metal coating, and (9) electroless nickel plating metal coating.

Silver, iron, nickel, or copper oxides may be used in method (1) above with subsequent reduction to the elemental metal. However, silver and copper oxides are easily wetted by metals and the reduction step is not always necessary.

Method (2) is similar to the formation of a cermet where there are two phases present, i.e. a ceramic and a metal phase.

In the third method the hydride of titanium or zirconium (or the elemental form) is used to wet the ceramic. As a rule the ceramic is coated with the hydride powder and the brazing alloy. The assembly is then brazed in vacuo or in a nonoxidizing atmosphere. During the brazing cycle the hydride dissociates into the pure metal and nascent hydrogen. The active metal, in conjunction with the molten brazing alloy, wets both the ceramic and the metal components. The copper-titanium eutectic produced by mixing 72% copper powder with 28% titanium hydride powder is a very popular brazing material¹. Other brazing composites using silver, copper, tin, nickel, and manganese are also used. Of the active materials, it appears that zirconium hydride gives the better bond to alumina⁴.

The bonds produced using a glaze containing metal powder are not considered satisfactory due to the brittleness of the glass phase.

The refractory metal process developed from the sintering of tungsten and molybdenum powders onto ceramic surfaces. Later the coatings were modified to include iron, manganese, and nickel. A typical coating is 4:1 molybdenum-manganese suspended in pyroxylin binder³. The coating is fired in a hydrogen atmosphere at 1350°C for one-half hour. The molybdenum coating is then nickel plated (or nickel is fired on) to give better wetting properties to the coating. Once the ceramic is metallized, the assembly is brazed using conventional brazing alloys.

Below are listed advantages and disadvantages of the three most popular brazing methods in use today¹:

I. The Molybdenum-Manganese Process

- A. Advantage - suitable for quantity production since the operation is insensitive to minor process variables.

B. Disadvantages

1. Multistep process (3 firings)
2. Hydrogen firing tends to discolor some ceramics and may harm their electrical properties.
3. Requires high firing temperature.

II. The Hydride Process

A. Advantages

1. Strong bonding.
2. Low firing temperature.
3. Can be bonded in a single operation using silver, copper, lead or other solders.
4. Fast brazing cycle.
5. Can be brazed in vacuum or an inert atmosphere instead of in hydrogen.
6. Gives better outgassing if brazed in vacuum (high chromium alloys can be used).

B. Disadvantages

1. High solder fluidity at the alloying temperature (physical dimensions of braze area are difficult to control).
2. Coating of the ceramic surface with an uniform layer of hydrides requires skillful hand work.

III. The Active Metal Process

A. Advantages

1. Extremely simple and easy process.
2. Good reproducibility.
3. Strong bond.

B. Disadvantages

1. Capillary considerations control the allowable design
2. Flow difficult to limit and control

The active metal or hydride processes are more corrosive to the ceramic than the refractory metal process, and they penetrate to a greater depth. The manganese in the refractory process partially oxidizes and forms manganese aluminate spinel, which in turn sinters to the molybdenum.

Some metals will adhere directly to ceramic bodies with little or no special surface preparation. Some of these metals are silver, copper, gold and platinum. These metals are usually painted onto

the ceramic from a solution containing an organic medium and a small amount of a low melting glass. The coating is usually very thin after firing and requires some additional plating prior to brazing.

Vapor desposited coatings are usually applied by spraying a volatile chloride in hydrogen from a burner nozzle onto the ceramic surface. The metal chloride and the hydrogen react to produce the metal at the surface which is to be metallized. Once the ceramic is metallized, it is then brazed in conventional manner.

Flame sprayed coatings may be used to metallize ceramic surfaces but much care must be exercised in the selection of materials and spraying procedures. A good coating might be applied by using a plasma jet sprayer.

Electroless nickel plating of ceramic materials is relatively new. The bond is more mechanical than chemical. The process does not require a high firing temperature to metallize the ceramic and may find wide usage in electronic printed circuitry.

Ceramic adhesives will resist higher temperatures than presently known organic adhesives. Use of ceramic adhesives should also result in a cost reduction over use of metal brazing. Ceramic adhesives are modified porcelain enamels to which metal powders and other compounds are added to reduce the brittleness of the bond. Generally, the adhesives are made from silicate glasses that are fritted, quenched, and ground in ball mills to form a slip. The application to metal may be done by dipping, rolling, or spraying. The metals are bonded by firing at elevated temperatures under pressure.

It is believed that higher strengths may be obtained for ceramic adhesives by (1) prefiring the adhesive to the coupons before bonding, (2) roughening the metal surfaces as much as possible, (3) using adhesives having a slightly lower thermal expansion than the metal (4) using a thin adhesive line, (5) increasing the wettability of the adhesive, (6) increasing the elasticity of the adhesive, and (7) adding active hydride powders to the adhesive.

The University of Illinois (Dept. of Ceramic Engineering) has conducted the majority of work on ceramic adhesive development. They have developed several adhesives which have been, and are being investigated by other agencies. One of these adhesives was selected for study under this program.

The first ceramic materials required as outer components of aircraft will probably be used as radomes or wave guides. Therefore, alumina and pyroceram were selected as the primary ceramic materials to be used in this investigation because they exhibit the desired electrical and mechanical properties and have good high temperature resistance. Kovar "A" was chosen as one of the metals for investigation because its thermal expansion closely matches the selected ceramics. The remaining materials were chosen as the need arose to accomplish the objectives of the research program.

MANUFACTURING RESEARCH - BONDING - CERAMIC-TO-METAL

OBJECT:

To investigate and develop methods for bonding ceramics to metals and metals to metals using ceramic adhesives and brazing alloys.

DESCRIPTION OF SPECIMENS, MATERIALS, AND EQUIPMENT

<u>I. Specimens</u>	<u>Source</u>
96% Al ₂ O ₃ with one surface metallized with Molybdenum-manganese alloy	Coors Porcelain Co. Golden, Colorado
Kovar "A" Iron Nickel Alloy	Carborundum Co. Niagara Falls, N.Y.
9606 Pyroceram	Corning Glass Co. Corning, N. Y.
High Expansion Pyroceram	"
17-7PH Cond. TH1050 Stainless Steel (FMS-0037)	Plaht Stock
Rene'41 Nickel Alloy	General Electric Co. Detroit, Michigan
Fiberfrax F-100 block	Carborundum Co. Niagara Falls, N.Y.
<u>II. Materials</u>	
71.5 Ag-28Cu-.5Li Brazing Alloy (0.003" foil)	Handy & Harman Bridgeport, Penn.
Cu, pure (0.0015" foil) QQ-C-502	Convair Stock
97.5 Ag -.3 Mg-.2 Ni-2.0 Li Brazing Alloy (0.003" foil)	Handy & Harmon Bridgeport, Penn.
"Nicro"-Ni-Au Alloy -150 mesh	Western Gold and Platinum Co. Belmont, Calif.
Aluminum Oxide 200 mesh	Carborundum Co. Niagara Falls, N.Y.
Titanium Chips	Republic Steel Corp. Massillon, Ohio

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II. Materials

Source

Synar Binder and Activation 23	Penn Salt Co. Philadelphia, Pa.
Ethyl Silicate	"
QM-105 Cement	Carborundum Co. Niagara Falls, N.Y.
5210 Frit	Solar Aircraft Co. San Diego, Calif.
Phosphoric Acid	Fisher Scientific Co. St. Louis, Mo.
Silicon Dioxide	"
Aluminum Oxide Powder	"
Silicon Powder	"
Boric Acid	"
Borax	"
Benzene	"
Sodium Nitrate	"
Lead Carbonate	"
Beryllium Sulphate	"
Cobalt Oxide	"
Ferric Oxide	"
Hydrofluosilicic acid	"
Stainless Steel Powder	Metal Disintegrating Co. Elizabeth, N.J.
Titanium Hydride	"
Zirconium Hydride	"
Copper Powder 200 Mesh	"
Nickel Foil (2 mil perforated)	Titanium Alloy Mfg. Co. Niagara Falls, N.Y.
M. F. Acid	Wyandotte Chemical Co. Wyandotte, Mich.

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II. Materials

Source

Silver Paint #543

Engelhard Industries, Inc.
East Newark, N.J.

Equipment

Sand Blasting Machine

Ruemelin Mfg. Co.
Milwaukee, Wis.

Vapor Degreaser

Convair Built

Tube Furnace

Lindberg Engineering Co.
Chicago, Ill.

Muffle Furnace

"

Ball Mill Rack

U. S. Stoneware Co.
Akron, Ohio

Ball Mills

McDaniel Refractory Porcelain Co.
Beaver Falls, Penn.

Temperature Strip
Recorder and Controller

Leeds & Northrop Co.
Philadelphia, Pa.

Universal Test Machine

Baldwin Co.
Waltham, Mass.

Tube Furnace

Morashall Products Co.
Columbus, Ohio

PROCEDURE:

The research program was conducted in three parts. These were as follows:

- I. Investigation of Ceramic-to-Metal Brazing
- II. Investigation of Ceramic-to-Metal and Metal-to-Metal Bonding With Ceramic Adhesives
- III. Investigation of Ceramic-to-Metal Mechanical Attachments

The detailed procedures used in each part of the program are given below.

I. Investigation of Ceramic-to-Metal Brazing

Small ceramic specimens of 96% alumina, having the dimensions given in Figure 2, were vendor metallized by the molybdenum-manganese process. Metallizing was applied only on the surfaces which were later to be brazed. The metallized area of the specimens was given a light sand blasting with 200 mesh alumina powder, and then electrolytically nickel plated to a thickness

of approximately one mil by conventional plating procedures.

A brazing jig was fabricated from Kovar "A" alloy. The jig was machined such that it aligned and held two of the metallized pieces of alumina in proper position to be brazed together. Washers were cut from 0.032" Kovar "A" sheet stock and from foils of the various brazing alloys. These washers had the same dimensional surface area as the metallized portion of the ceramic pieces.

The metallized alumina specimens were vapor degreased after nickel plating was applied. Kovar washers were cleaned by a 3 minute immersion in concentrated nitric acid, rinsed in tap water, and dried. The brazing alloy washers were given a 30 second dip in 50% by volume hydrochloric acid, rinsed in tap water, and dried.

Each tensile specimen was fabricated by brazing a metallized alumina piece to each side of a Kovar washer. The assembly was set up for brazing by placing one piece of the alignment jig upon a table, and in successive order, slipping one metallized alumina specimen, a brazing alloy washer, a Kovar washer, another brazing alloy washer, and another metallized alumina specimen into the alignment jig. The other end of the alignment jig was then placed on the assembly and screwed down hand tight, being careful to keep the three washers in good alignment with the two pieces of ceramic. An exploded view of the components for such an assembly is shown in Figure 3. The photograph also shows an assembled tensile specimen ready for brazing, one which has been brazed, and one on which the bonding cups have been added to testing in tension.

All brazing (except when using gold-nickel braze alloy) was done in a double tube furnace. Purified argon was used as the brazing atmosphere in these experiments. The argon, regulated at 10 psi, passed through a flow meter at a rate of 200 cubic inches per hour into a dry ice-acetone moisture trap, through the first furnace tube which contained titanium chips to remove oxygen, and finally into the second furnace tube which was the brazing chamber. The furnace and accessories are shown in Figure 4. Specimens to be brazed were placed in a small "boat" which was manually manipulated into proper position in the furnace by means of a long wire handle which had been welded to the boat. A controlling thermocouple was also attached to the boat. Temperatures were read on a strip recorder.

With argon flowing and the furnace temperature stabilized at the desired point for brazing, each assembly was loaded horizontally into the boat and placed into the hot zone of the furnace. After 15 minutes brazing time the assembly was moved from the hot zone to a cooler zone of the tube and allowed to cool to 500°F (or below) before being removed from the argon atmosphere. This procedure was used on all tensile specimens

with the exception of specimens 11-19 and specimens 25-41. The latter group of specimens were made by giving the nickel plated ceramic a very light sandblasting before the vapor degreasing step. Otherwise they were treated in the same manner described above.

Specimens 11-15 were brazed with a powdered gold-nickel alloy which had to be applied to the metallized ceramic in a different manner. The brazing alloy was applied as a borax suspension which was allowed to dry and was then fired 10 minutes at 1350°F in an argon atmosphere. The borax melted and held the alloy to the metallized surface of the ceramic. Much difficulty was encountered in forming a uniform coating of the alloy. The assembly of the components was then made on the alignment jig as before, except no brazing alloy washers were used. The assembly was placed in a vertical position within a muffle box which was equipped for introduction of purified argon. As before, the argon passed over titanium chips to remove oxygen. Brazing was carried out in a muffle furnace in a similar manner to that used with the double tube furnace.

Specimens 16-19 were metallized with a silver paint after the molybdenum-manganese coatings had been ground off and the ceramics vapor degreased. The silver paint (Hanover No. 543) was brushed on the ceramic and fired at 1500°F for 15 minutes. The specimens were then brazed as previously noted.

Two types of pulling jigs were used in the tensile testing of the brazed specimens. One employed the use of pulling blocks or cups which were bonded to the unmetallized ends of the alumina specimens with TY-85 adhesive (see Figure 3). This jig was used for most of the room temperature tensile tests. Some of the room temperature and all of the elevated temperature tests were conducted with a mechanical gripping jig. The machining of the jig was an extremely difficult operation and the finished product did not hold the specimens in perfect alignment. As the specimens were pulled it was visibly evident that they were allowed to "cock" in the jig.

Several other experiments were conducted in brazing ceramics to metals. This work was mainly in metallizing the ceramics by methods other than the molybdenum-manganese method. The experiments briefly were as follows: (1) Pyrocera 9606 and high expansion pyrocera were metallized by the titanium and zirconium hydride processes and brazed to Kovar using copper, silver-copper, and gold-nickel brazing alloys in an argon atmosphere, (2) same as (1) above except the ceramic was 96% alumina, (3) alumina was metallized by flame spraying nickel-chromium, (4) alumina was metallized by the silver paint process and brazed to Rene'41 with a silver-copper brazing alloy under argon and (5) alumina was electroless nickel plated and brazed to Rene'41 with a silver-copper braze alloy under argon. None of the specimens were pulled in tension.

II. Investigation of Ceramic-to-Metal and Metal-to-Metal Bonding With Ceramic Adhesives

A. Cleaning Adherends Prior to Bonding

1. 17-7PH Cond. TH1050 Steel

- a. Remove heat-treat scale by by vapor-honing with #120 aluminum oxide grit.
- b. Wipe with methyl-ethyl ketone.
- c. Vapor degrease with stabilized trichloroethylene.
- d. Immerse in the following solution for 4 minutes at 135°F.

MF Acid* 59.5 grams
(70%) Nitric Acid 170 milliliters
Tap water to make one liter of solution

- e. Rinse in running tap water.
- f. Immerse in the following solution for 5 minutes at 160°F.

Sodium Dichromate 113 grams
(96.6%) Sulphuric Acid 282 grams
Tap water to make one liter of solution

- g. Rinse in running tap water.
- h. Distilled water spray rinse.
- i. Dry at 160°F for 20 minutes.

2. Perforated Nickel Foil (2 mil)

- a. Wipe with methyl-ethyl ketone.
- b. Vapor degrease with stabilized trichloroethylene.
- c. Immerse in the solution designated in "A.1.f" above for one minute.
- d. Rinse in running tap water.
- e. Distilled water spray rinse.
- f. Dry at 160°F for 20 minutes.

3. Kovar Steel

- a. Wipe with methyl-ethyl ketone.
- b. Vapor degrease with stabilized trichloroethylene.
- c. Immerse in the following solution for 5 minutes at room temperature.

(70%) Nitric Acid 15% by volume
(50%) Hydrofluoric Acid 3% by volume
Tap water 82% by volume

* Proprietary Compound - Wyandotte Chemical Co.,
Wyandotte, Michigan

- d. Rinse in running tap water.
- e. Distilled water spray rinse.
- 4. Pyroceram
 - a. Vapor degrease with stablized trichloroethylene.
 - b. Air dry for one hour.
- 5. Alumina - Clean the same as Pyroceram in "A.4" above.
- 6. Fiberfrax - Clean the same as Pyroceram in "A.4" above.
- 7. Rene' 41
 - a. Follow steps listed in Paragraph "A.1" above except immerse in the cleaning solution for 30 minutes at 170°F.
 - b. Rinse in running tap water.
 - c. Distilled water spray rinse.
 - d. Dry at 160°F for 20 minutes.
- 8. RS-140 Solution - Treated and Aged Titanium Alloy
 - a. Remove heat-treat or aging scale by immersion in a "Virgo" salt bath.
 - b. Immerse in the following solution for 30 to 60 seconds at room temperature.

(70%) Nitric Acid	15% by volume
(50%) Hydrofluoric Acid	3% by volume
Tap water	82% by volume
 - c. Rinse in running tap water.
 - d. Immerse in the following solution for two minutes at room temperature.

Trisodium Phosphate	50 grams
Sodium Fluoride	8.9 grams
(50%) Hydrofluoric Acid	26 milliliters
Tap water to make one liter of solution	
 - e. Rinse in running tap water.
 - f. Immerse in running tap water for 15 minutes at 130-150°F.
 - g. Distilled water spray rinse.
 - h. Dry at 160°F for 20 minutes.

**Proprietary Process - Hooker Electrochemical Co.,
Niagara Falls, N.Y.

B. Adhesive Preparation Bonding and Testing

1. Air Setting Adhesives

a. Adhesive No. 1 - QM-105

- (1) Prepare various prime coats for the Rene'41 metal using Synar Binder plus Activator 23 as follows:
 - (a) Synar Binder plus 6% Activator 23.
 - (b) Synar Binder plus 6% Activator 23 plus 2% Hydrofluosilicic Acid.
 - (c) Synar Binder plus 6% Activator 23 plus 1% Ethyl Silicate.
- (2) Apply one thin coat of each prime coat to 1" square pieces of clean Rene'41.
- (3) Leave two specimens unprimed as controls.
- (4) Place one thickness of QM-105 adhesive between two pieces of metal for each of the prime conditions and dry as follows using contact pressure.
 - (a) Air dry for 1 hour.
 - (b) Oven dry for 2 hours at 160°F.
 - (c) Oven dry for 16 hours at 195°F.
- (5) Test for adhesion by peeling apart.
- (6) See Table III for results.

b. Adhesive No. 2- Synar Binder plus Activator 23

- (1) Prepare Synar adhesive as follows:

Synar Binder	-	20 parts by wt.
Activator 23	-	5 parts by wt.
Silicon Dioxide	-	100 parts by wt.
- (2) Apply and cure as for QM-105 adhesive above.
- (3) Test for adhesion by peeling apart.
- (4) See Table III for results.

c. Adhesive No. 3 - Aluminum Phosphate "A"

- (1) Prepare Aluminum Phosphate A adhesive as follows:

Aluminum Phosphate - 70 grams
Aluminum Oxide - 30 grams

- (2) Apply the adhesive to clean Rene'41 and low expansion Pyroceram.
- (3) Bond the Rene'41 and Pyroceram together using contact pressure and the following cure cycle:

4 hours at 160°F
16 hours at 800°F
1 hour at 1500°F

- (4) Test for adhesion by peeling apart.
- (5) See Table III for results.

d. Adhesive No. 4 - Aluminum Phosphate "B"

- (1) Prepare Aluminum Phosphate B adhesive as follows:

Aluminum Phosphate - 67 grams
Aluminum Oxide - 77 grams
Silicon Powder - 47 grams

- (2) Bond and test the same as for Adhesive "A" above except bond to Fiberfrax instead of Pyroceram.
- (3) See Table III for results.

2. Fired Adhesives

a. Adhesive No. 5- Frit 5210

- (1) Spray coat Rene' with 5210 adhesive slip.
- (2) Place the coated surfaces of two pieces of Rene'41 together and fire for 12 minutes at 1500°F with contact pressure.
- (3) Test for adhesion by peeling apart.
- (4) See Table III for results.

b. Adhesive No's 6, 7 & 8 - Frits 1, 2 & 3

- (1) Prepare three frits by smelting the following constituents:

Frit 1(smelt at 2300°F)	Frit 2(smelt at 1800°F)	Frit 3(smelt at 2710°F)
Silicon Dioxide 42%	Silicon Dioxide 18.3%	Silicon Dioxide 34.8%
Boric Acid 21.8%	Lead Carbonate 72.4%	Beryllium Sulphate 42.7%
Sodium Nitrate 36.2%	Sodium Nitrate 9.3%	Sodium Nitrate 22.5%

- (2) Prepare slips from the frits by adding water and ball milling for 4 hours.
- (3) Spray coat clean 1" squares of .064 gage Kovar steel and 1/2" low expansion Pyroceram and allow to dry for 1 hour at room temperature followed by 1 hour at 160°F.
- (4) Bond the coated parts together using contact pressure and the firing temperatures listed below:

Frit No.	Firing Temp.	Atmosphere
1	1550°F	Air
2	1200°F	Air
3	2100°F	Air
3(firing 2)	2100°F	Partial Argon
3(firing 3)	2150°F	Argon
3 Add 0.7% Cobalt Oxide (firing 4)	2200°F	Argon

- (5) Test for adhesion by peeling apart.
- (6) See Table III for results.

c. Adhesive No. 9- UI-1067-1A (University of Illinois)

- (1) Prepare UI-1067-1A adhesive frit by firing the following components at 1800°F for 2 hours followed by 2 hours at 2450°F:

Silicon Dioxide	- 24.8 parts by wt.
Sodium Nitrate	- 9.0 parts by wt.
Boric Acid	- 66.2 parts by wt.

- (2) Prepare UI-1067-1A slip by ball milling the following constituents for 4 hours.

Frit (UI-1067-1A)	100 parts by wt.
Syloid	2 parts by wt.
Water (distilled)	160 parts by wt.
Ferric Oxide	2 parts by wt.
Stainless Steel Powder	20 parts by wt.

- (3) Brush coat clean 1" squares of .064" Kovar and 1/2" high expansion Pyroceram with the UI-1067-1A slip and allow to dry for 1 hour at room temperature followed by 1 hour at 160°F.
- (4) Fire the separate specimens for 5 minutes at 1750°F.

First Bonding

- (5) Bond the coated Kovar to the coated high expansion Pyroceram for 12 minutes at 1750°F.

Second Bonding

Bond the same as for the first bonding except use a 2 mil perforated nickel carrier in the bond joint.

Third Bonding

Bond the same as for the first bonding except use 17-7PH-TH1050 stainless steel instead of Kovar.

Fourth Bonding

Bond the same as for the third bonding except use a 2 mil perforated nickel carrier in the bond joint.

- (6) Test for adhesion by peeling apart.

- (7) See Table III for results.

Fifth Bonding

Conduct the fifth bonding as follows:

- (a) Brush coat one side of one end (approx. 1/2" of 1" x 4" x .061" cleaned 17-7PH-TH1050 stainless steel with the UI-1067-1A adhesive slip.
- (b) Dry for 1 hour at room temperature followed by 1 hour at 160°F.
- (c) Fire separate specimens at 1750°F for 5 minutes.
- (d) Assemble the coated ends of two specimens such as to form a 1/2" single overlap.
- (e) Place in the bond fixture as shown in Figure 5.
- (f) Apply 40 psi air pressure to the pressure diaphragm (1/2 sq. in. diaphragm contact area produced 40 psi bond pressure).
- (g) Place the assembly in a furnace and fire at 1750°F for 12 minutes.
- (h) Remove from furnace and allow to cool below 1000°F before reducing the pressure in the diaphragm.

Note: Prepare the specimens containing a 2 mil perforated nickel carrier by placing the carrier in the bond joint prior to bonding.

(i) Test in shear at a load rate of 1300 pounds per minute per square inch bond area.

(j) See Table IV for results.

Note: Sixth Bonding

(a) Conduct the sixth bonding in the same manner as the fifth bonding except use RS-141 titanium skins.

(b) See Table V for results.

III. Investigation of Ceramic-to-Metal Mechanical Attachment

A 0.500" x 8.0" x 12.0" pyroceram 9606 plate was mechanically attached and sealed to a chamber made from 17-7 stainless steel using a design suggested by Inglis¹⁶. The box was so designed that the ceramic formed one side of the chamber (see Figures 6 and 7). The chamber was provided with inlet and outlet tubes, valves, gauges, and a pressure regulator to enable air pressurization of the chamber.

A 0.032" thick soft copper gasket was used as a seal and the pyroceram plate was bolted to the steel chamber. The chamber was then pressurized to 5 psi by regulation of the valves on the inlet and outlet air lines. The assembly was then placed in an electric resistance furnace and heated to 1500°F in six hours. The pressure in the chamber was maintained at 5 psi by regulation of the valves and air regulator until a leak developed in the gasket. After the leak occurred the pressure was maintained as near 5 psi as regulation would allow. After completion of the run the assembly was allowed to cool to room temperature. It was then inspected for cracks or other damage.

RESULTS:

The results of room and elevated temperature tensile tests on brazed alumina-Kovar specimens are given in Table I.

Table II lists the results of laboratory applied metallizing and brazing experiments on alumina and pyroceram.

The adhesion characteristics of bonded ceramics tested at room temperature are given in Table III.

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Tables IV and V list room and elevated temperature lap shear test results on UI-1067-1A bonded 17-7PH stainless steel and RS-140 titanium, respectively.

The mechanical attachment assembly held the 5 psi design pressure until a temperature of 1200°F was attained. At that temperature the gasket developed a leak and the pressure could no longer be maintained at 5 psi within the chamber. At 1500°F the outlet pressure had decreased to 3.5 psi for an inlet pressure reading of 5.5 psi. The pyroceram and the 17-7 steel chamber were not visibly harmed by the temperature-pressure exposure.

DISCUSSION

The ceramic-to-metal attachments made by brazing procedures look very promising. The quality of the attachments was determined by the load required to cause failure of the joint in tension. The load values marked with an asterisk in Table I were obtained by use of a mechanical gripping type pulling jig. The jig was designed to allow pulling of specimens at elevated temperatures. The standard bonded cup type pulling jig was used to pull approximately half of the room temperature specimens. The bonded cup jig was unsuitable for use at elevated temperatures since the adhesive used to bond the pulling blocks to the specimens would not take the temperature.

Note in Table I that the higher values for room temperature tests were obtained primarily when using the bonded cup type jig. Unfortunately, the mechanical gripping type jig was found to be pulling specimens slightly off center. The jig was reworked several times but proper alignment of the specimens was never achieved. The time element was such that a new jig could not be designed and fabricated in time to be used in this program. Therefore, the mechanical gripping device was used even though the alignment of specimens in the jig was poor. The effect of the misalignment can be seen in Table I by comparing room temperature values of similar specimens pulled by both type of jigs.

Specimens 1-5 were brazed with a low melting silver solder selected to represent a silver-copper alloy and were not expected to have high temperature properties. The solder might find use where lower brazing temperatures are desired and service temperatures are moderate.

Specimens 6-10 were brazed with an alloy containing 97.5% silver. It was selected for high temperature strength. When the alloy was used it was noted that the ceramic contained a black coating on the surface. Attempts to identify the black deposits by X-ray diffraction procedures were not successful. The same coating was noted on specimens 1-5 but to a much lesser extent. The single specimen pulled at 1200°F failed at approximately the same loading as the specimens pulled at room temperature.

Specimens 11-15 used a gold-nickel eutectic alloy selected for high temperature strength and oxidation resistance. Extreme difficulty was encountered in applying the alloy because it was a rather coarse powder. This made it virtually impossible to obtain a brazed coating of the desired thickness and uniformity. The alloy on these specimens was much too thick and ran to the sides and out of the braze area. It is felt that much higher results might be expected from this alloy if the material was used in foil form.

Specimens 16-19 were metallized with a liquid silver paint and later brazed with silver-copper-lithium alloy. The specimens could be broken by hand after brazing. From visual observations of the specimens it was concluded that the brazing temperature used was too high for the metallizing. The brazing alloy took the silver into solution. It is believed that much better results might be obtained by electroplating additional silver on the metallizing prior to brazing, and later brazing at a lower temperature.

Specimens 20-41 were brazed with pure copper. The copper was selected for its high temperature strength, and more important, its ability for plastic deformation. It was hoped that the copper would deform and flow enough to relieve the thermal stresses set up by differences in thermal expansion between the Kovar and the alumina. The strength values for the copper brazes exceeded expectations.

All specimens (except as noted in Table I) failed at the ceramic-metallize interface. This indicates that the weakest part of the ceramic-to-metal joints was the adhesion of the molybdenum-manganese metallize to the alumina. This prompted the limited investigation of several other metallizing methods. Due to lack of time in this program none of the laboratory metallized specimens were pulled in tension. However, visual observations of the specimens revealed the active hydride process caused the metallize to penetrate deeper into the ceramic surface than the other processes. This was expected since the literature survey (see Introduction) revealed that greater strengths should be obtained by the active hydride process due to its penetration into the ceramic. The electroless nickel plating process also looked good for low temperature work. A drawback of the process might be that only a mechanical type of adhesion is obtained and the peel strength might not be as good as desired.

The laboratory metallizing experiments, though limited, show that better adhesion can be expected between the ceramic and the metallized coating by the use of procedures other than the molybdenum-manganese process. It is definitely felt that the active metal and active hydride processes and the electroless nickel process should receive further investigation.

All of the ceramic-to-metal specimens bonded with ceramic adhesives

were considered as screening or "look-see" specimens. Real strength was not expected due to the brittle nature of the bond. All the specimens could be broken by hand after bonding. Therefore, it is evident that this type of bond cannot be used for aircraft construction in areas where high strengths are required.

The work on metal-to-metal bonding with ceramic adhesives shows that fair to good shear strengths are attainable at temperatures up to 1000°F. Tables IV and V show lap shear test results for UI-1067-1A bonded 17-7PH stainless steel and RS-140 titanium, respectively. The University of Illinois adhesive was developed as part of their research program on adhesives requiring shear strengths of 1000 psi or better at temperatures up to 1000°F. It is not expected that the adhesive will exhibit much strength above 1100°F because the softening point of the glass occurs near that temperature.

The objectives of the mechanical attachment experiment were arbitrarily selected to be the attachment of a ceramic plate to a metal chamber in such a way that the assembly would withstand 5 psi internal pressure at temperatures up to 1500°F. The assembly was designed by the Structures Group of the Engineering Test Laboratory. The assembly held up well at temperatures up to 1200°F, but at that point the gasket began leaking and the internal pressure could not be maintained at 5 psi for higher temperatures. The 1500°F exposure did no physical damage to the ceramic-steel attachment itself. Actually the chamber was so designed that the ceramic received very little loading. No particular strength to weight considerations were used. It is felt that the mechanical attachment of ceramic-to-metal on a strength to weight basis would leave much to be desired, and that a superior attachment can be made by brazing or bonding methods.

CONCLUSIONS AND RECOMMENDATIONS

The bonding of ceramics to metals and metals to metals with ceramic adhesives and brazing alloys was investigated. The results of this research program show that ceramics can be successfully attached to metals by brazing, bonding, and mechanical methods, and that the assemblies are capable of withstanding temperatures of 1000-1500°F with fair to good strength. Of the three attachment methods investigated, the brazing method looks most promising. Limited studies of various metallizing processes for ceramics indicate that greater adhesion can be expected between the ceramic and the metallized coating through the use of a metallize process which penetrates deeper into the ceramic surface.

It is recommended that further research be conducted at Convair to determine or develop the following:

- (1) The size-strength relationship of ceramic-to-metal attachments by fabrication and testing of larger specimens.
- (2) The merits of the active metal and hydride processes and the electroless nickel process for metallizing various ceramics for

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subsequent brazing to other metals and ceramics.

- (3) Brazes capable of exhibiting good strength at temperatures up to 2000°F.

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FIGURE 1

INTERNAL EXPANSION CURVES FOR VARIOUS MATERIALS^{15,16}

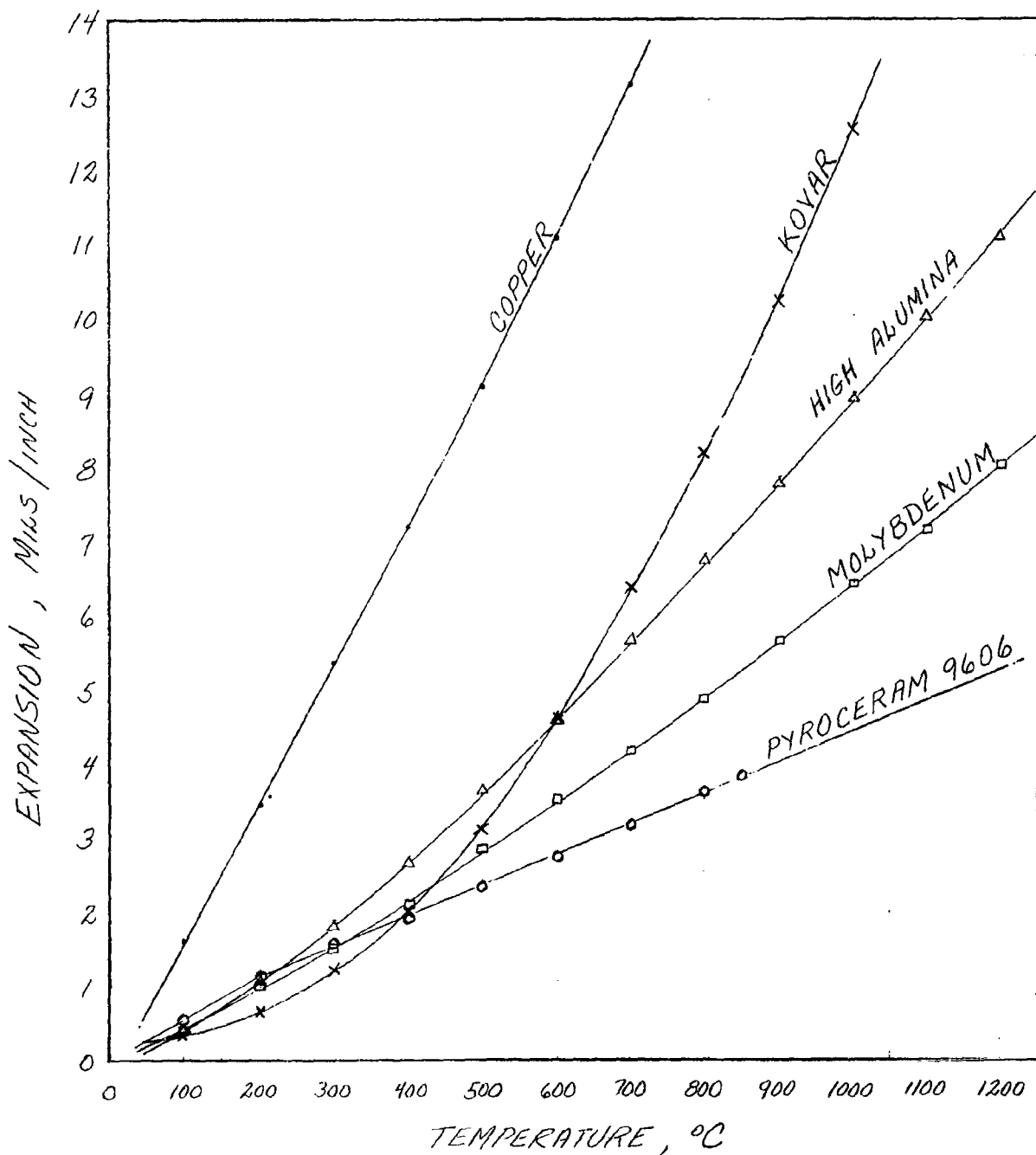
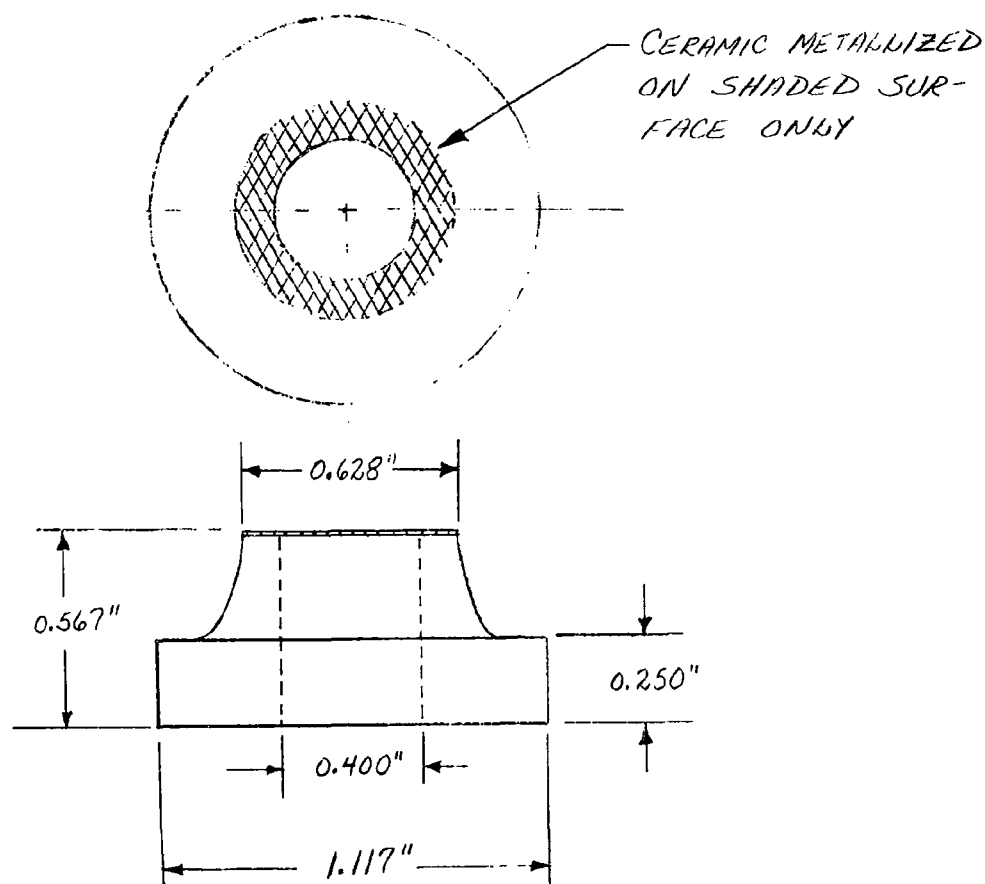


FIGURE 2

CERAMIC TENSION TEST BRAZING SPECIMEN



CERAMIC: 96% Al_2O_3

METALLIZE: MOLYBDENUM-MANGANESE

MFG. BY COORS PORCELAIN CO.
GOLDEN, COLORADO



FIGURE 3

PREPARATION OF BRAZING
SPECIMENS FOR TENSION TEST
F-8380
CONVAIR FT. WORTH TEXAS

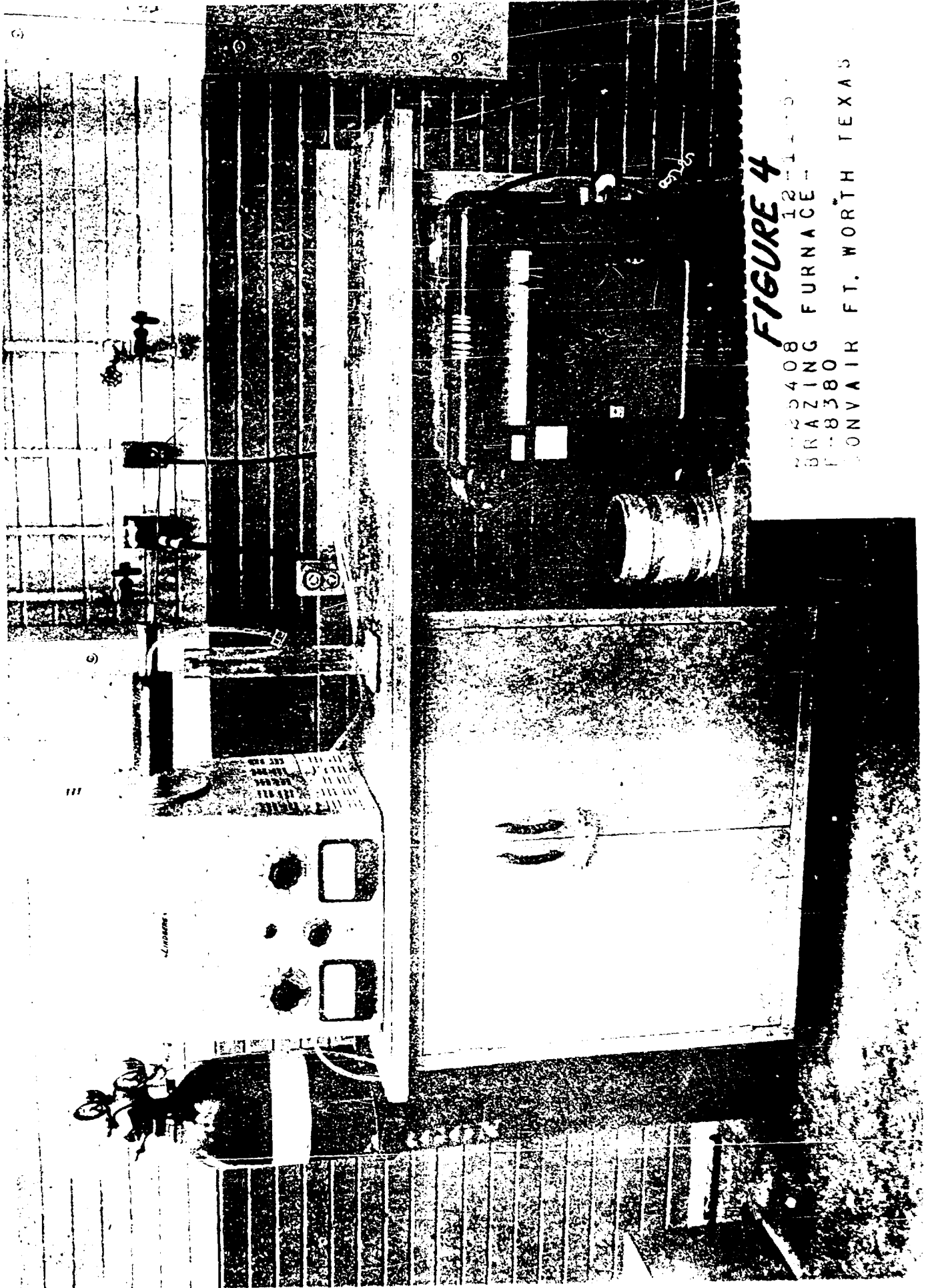


FIGURE 4

12-1-59
BRAZING FURNACE -
F-8380
CONVAIR FT. WORTH TEXAS

FIGURE 5



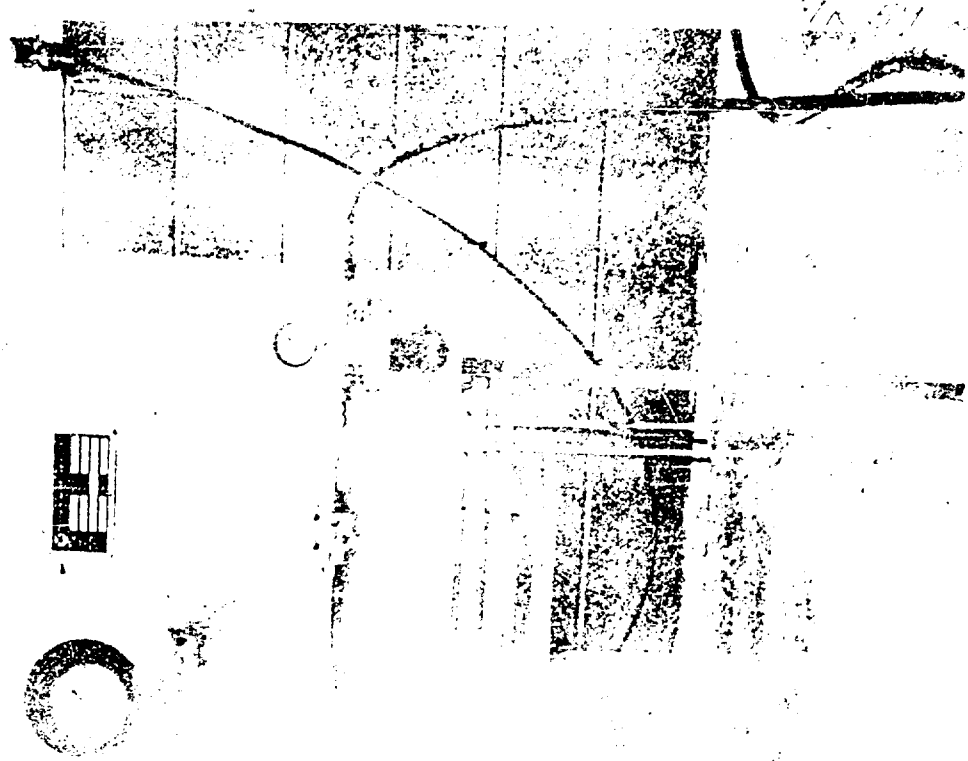


FIGURE 6

AMERICAN METAL
ANNUAL ATTACHMENT
1980
ATLANTA, GEORGIA
NORTH TEXAS

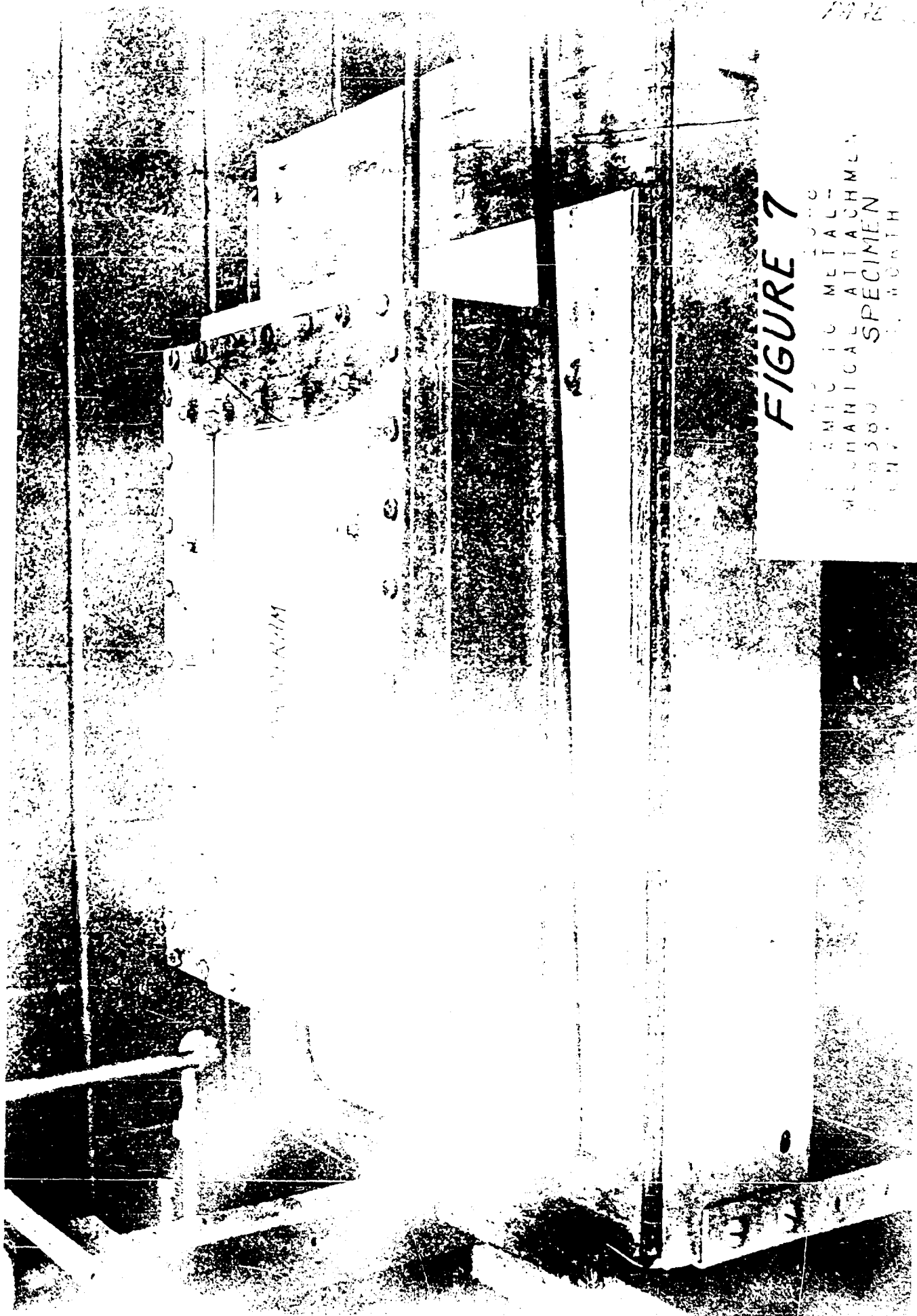


FIGURE 7

MECHANICAL ATTACHMENT
SPECIMEN
100380
100380

TABLE I
RESULTS OF TENSILE TESTS ON ALUMINA - KOVAR "A" BRAZES

SPECIMEN No.	TYPE OF METALLIZING USED ON ALUMINA	TYPE OF PLATING OF METALLIZED SURFACE	TYPE OF BRAZING METAL USED	BRAZING TEMP, °F (15 MINUTES)	TENSILE LOADING TEMP, °F	LOAD AT FAILURE, PSI	REMARKS
1	Mo-MN	NICKEL	Ag-Cu-Li	1610	R.T.	4060 *	AVG. BY MECHANICAL GRIPPING JIG = 4077 PSI
2	"	"	"	"	"	5410 *	
3	"	"	"	"	"	2760 *	
4	"	"	"	"	"	4410	
5	Mo-MN	NICKEL	Ag-Mn-Ni-Li	1610	R.T.	6910	AVG. BY BONDED CUP JIG = 5660 PSI
6	Mo-MN	NICKEL	Ag-Mn-Ni-Li	2000	R.T.	2430 *	R.T. AVG. BY MECHANICAL GRIPPING JIG = 2283 PSI
7	"	"	"	"	"	3490 *	
8	"	"	"	"	"	930 *	
9	"	"	"	"	R.T.	5940	
10	"	NICKEL	Ag-Mn-Ni-Li	2000	1200	2190 *	BAD BOND
11	"	Ni	Ag-Ni	2050	"	9760	
12	"	"	"	"	R.T.	432 *	
13	"	"	"	"	1500	842	
14	"	NICKEL	Ag-Ni	2050	R.T.	842	HAD BEAD ON SIDE
16-19	LIQUID AG	NONE	Ag-Cu-Li	1600	"	"	ALL BAD BRAZES
20	Mo-MN	NICKEL	Cu	2000	R.T.	4650 *	R.T. AVERAGE = 8493 PSI
21	"	"	"	"	"	3940 *	
22	Mo-MN	NICKEL	Cu	2000	R.T.	4180 *	
25	Mo-MN	NICKEL **	Cu	2000	R.T.	8750	
26	"	"	"	"	"	11700	CERAMIC BROKE
27	"	"	"	"	"	6370	
28	"	"	"	"	"	5780	
29	"	"	"	"	"	9360	
30	Mo-MN	NICKEL **	Cu	2000	"	9280	CERAMIC CRACKED
31	"	"	"	"	R.T.	9610	
32	"	"	"	"	1200	3160 *	
33	"	"	"	"	1200	3160 *	
34	"	"	"	"	1500	5510 *	CERAMIC CRACKED
35	"	"	"	"	1500	2270 *	
36-41	Mo-MN	NICKEL **	Cu	2000	"	"	CERAMIC CRACKED

* USED MECHANICAL TYPE GRIPPING JIG (USED BONDED CUP TYPE JIG ON OTHER SPECIMENS).
** PLATING GIVEN SLIGHT SAND BLAST BEFORE BRAZING OPERATION.

NOTES: (1) ALUMINA PIECES WERE METALLIZED ONLY ON FACES TO BE BRAZED.
(2) SPECIMENS NOS. 15, 23 & 24 WERE LOST.

ABBREVIATIONS:

R.T. - ROOM TEMPERATURE
Mo - MOLYBDENUM
Mn - MANGANESE
Ag - SILVER

Cu - COPPER
Li - LITHIUM
Ni - NICKEL
Au - GOLD

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TABLE II

RESULTS OF LABORATORY APPLIED METALLIZING AND BRAZING RUNS ON ALUMINA AND PYROCERAM

CERAMIC	METALLIZING PROCESS	BRAZED TO	BRAZING ALLOY	RESULTS (Visual Observations)
96% Alumina	Zirconium Hydride	Kovar	Ag-Cu	Good adherence & braze
"	Titanium	"	"	"
"	"	"	Cu	"
"	"	"	Au-Ni	"
Pyroceram 9606	"	"	"	Ceramic chipped* Out in Braze Area
"	"	"	"	"
"	"	"	Cu	"
"	Zirconium	"	"	"
High Expansion Pyroceram	"	"	"	"
"	Titanium	"	"	"
"	"	"	"	"
96% Al ₂ O ₃	Flame Sprayed Ni-Cr	"	Ag-Cu	Ni-Cr did not adhere
"	Electroless Nickel Plating	Reco 141	Not brazed	Good adherence & braze
"	Silver Paint	"	Ag-Cu	Fair adherence & braze

*Note: Chipping caused by combination of following:

- (1) Differences in thermal expansion of ceramic and metal.
- (2) Joints had greater strength than ceramic itself.

TABLE III
ADHESION CHARACTERISTICS OF BONDED CERAMICS TESTED
AT ROOM TEMPERATURE

ADHESIVE NO.	ADHESIVE TYPE	ADHERENDS	ADHESION CHARACTERISTICS
1 (no prime)	QM-105	Rene '41 to Rene '41	Poor adhesion
1 {prime 1}	"	"	Fair "
1 {prime 2}	"	"	Good "
1 {prime 3}	"	"	No "
2	Synar	"	No "
3	Alum. Phosphate "A"	" to low exp. Pyroceram	No "
4	Alum. Phosphate "B"	" to Fiberfrax	Dry powder formed, no adhesion
5	Frit 5210	" to low exp. Pyroceram	No adhesion
6	Frit 1	Kovar to Alumina	Good adhesion- withstood five F.T. to 1000°F cycles without spalling
7	Frit 2	"	Same as Frit 1
8 {Firing 2}	Frit 3	"	Fair adhesion
8 {Firing 3}	Frit 3	"	Fair adhesion
8 {Firing 4}	Frit 3	"	Fair adhesion
9 (First Bond)	UI-1067-1A	Kovar to high exp. Pyroceram	Fair adhesion to Kovar, good adhesion to Pyroceram. Pyroceram broke apart upon cooling.
9 (Second Bond)	UI-1067-1A	"	Same as First Bond above
9 (Third Bond)	"	17-PH-TH1050 Stain- less Steel to high exp. Pyroceram	Good adhesion to both 17-7PH-TH1050 steel and Pyroceram but Pyroceram broke apart upon cooling.
9 (Fourth Bond)	"	"	Same as Third Bond above.

TABLE IV

LAP SHEAR STRENGTH OF UI-1067-1A (ADHESIVE NO. 9, FIFTH BONDING) BONDED
17-7PH-TH1050 STAINLESS STEEL

SPECIMEN NO.	BONDED AREA (IN.) ²	COH. FAILURE (%)	LOAD (LBS)	TO FAILURE (PSI)
-----------------	-----------------------------------	---------------------	---------------	---------------------

TESTED AT ROOM TEMP. (NO OVEN AGE)

1	.535	0	725	1355
2	.570	0	580	1023
3	.550	0	775	1400
4S*	.520	45	613	1180
Average				1240

TESTED AT 1000°F AFTER 1/2 HOUR AT 1000°F

5S*	.500	70	1090	2180
6	.592	0	1260	2128
7	.551	5	1765	3203
8	.550	0	1500	2727
Average				2560

TESTED AT ROOM TEMP. AFTER 200 HOURS AT 1000°F

9S*	.533	85	800	1501
10	.540	2	1075	1991
11	.530	5	1115	2104
12	.532	2	1080	2070
Average				1905

TESTED AT 1000°F AFTER 200 HOURS AT 1000°F

13S*	.557	2	880	1580
14	.536	0	875	1632
15	.518	0	1370	2645
16	.526	0	1120	2129
Average				1995

* = 2 mil perforated nickel carrier used in bond joint

Note: The bond line thickness averaged 3 mils with no carrier and 5 mils with carrier.

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TABLE V

LAP SHEAR STRENGTH OF UI-1067-1A (ADHESIVE NO. 9 SIXTH BONDING)
BONDED RS-140 TITANIUM

SPECIMEN NO.	BOND AREA (IN.) ²	COH. FAILURE (%)	LOAD TO FAILURE (LBS)	LOAD TO FAILURE (PSI)
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TESTED AT ROOM TEMPERATURE (NO OVEN AGE)

1	.500	0	380	760
2S*	.600	5	567	945
Average				853

TESTED AT 1000°F AFTER 1/2 HOUR AT 1000°F

3S*	.498	50	1085	2179
4	.511	0	1165	2281
Average				2230

TESTED AT ROOM TEMPERATURE AFTER 200 HOURS AT 1000°F

5S*	.540	2	515	954
6	.524	2	455	868
Average				911

TESTED AT 1000°F AFTER 200 HOURS AT 1000°F

7S*	.467	5	1125	2409
8	.523	2	1375	2629
Average				2519

* = 2 mil perforated nickel carrier used in bond joint.

Note: The bond line thickness averaged 3 mils with no carrier
and 5 mils with carrier.